DIFFERENT COATING TYPE ON COPPER SUBSTRATE

by

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Thesis is submitted in partial fulfillment of the requirements
for the award of degree of
Bachelor of Mechanical Engineering with Automotive Engineering

Faculty of Mechanical Engineering
UNIVERSITI MALAYSIA PAHANG

JUNE 2013

ABSTRACT

This thesis will deal with the effect of different coating types on solder joint strength, specifically on intermetallic compound (IMC). Coating is essential in printed circuit board application since it can protect the base material, which is Copper, from oxidation and degradation. However, the coating thickness will give different effect on solder joint strength or life. Two types of surface finish have been used in this research which is Electroless Nickel and Electroless Nickel / Immersion Gold (ENIG). The purposes of the surface finish are to provide a diffusion barrier, oxidation barrier, adhesion and solderable surface on copper substrate. For this research, solder material that will be used is Sn-4Ag-0.5Cu to form a solder joint. All samples were subjected to reflow soldering and then to the isothermal ageing at 150℃ with duration 250 hours and 500 hours. The IMCs were characterized using scanning electron microscopy and image analyser to investigate the thickness of IMC on solder joint at all samples. From the research, it was observed that the IMC growth is influenced by ageing duration where the thickness of IMC is increases with ageing.

ABSTRAK

Tesis ini akan membincangkan tentang kesan lapisan salutan yang berbeza terhadap kekuatan sambungan solder terutamanya terhadap sebatian antara logam (IMC). Lapisan salutan amat penting terhadap aplikasi di dalam papan litar kerana ianya mampu melindungi bahan asas papan litar tersebut iaitu kuprum daripada pengoksidaan dan kemerosotan. Walaubagaimanapun, ketebalan lapisan salutan boleh memberi kesan yang berbeza terhadap kekuatan sambungan solder dan jangka hayatnya. Dua jenis permukaan penyudahan digunakan dalam penyelidikan ini iaitu *Electroless Nickel* dan *Electroless Nickel / Immersion Gold* (ENIG). Tujuan penyudahan permukaan adalah untuk memberi halangan terhadap penyebaran, halangan pengoksidaan, lekatan dan memberi keboleh solderan di atas substrak kuprum. Semua sampel akan dikenakan pematerian *reflow* sebelum dikenakan penuaan isoterma pada suhu 150℃ selama 250 jam dan 500 jam. IMC akan dikarakterkan menggunakan SEM dan penganalisis gambar untuk mencari ketebalan IMC pada sambungan solder di setiap sampel. Daripada penyelidikan, didapati pembentukan IMC dipengaruhi oleh masa penuaan isoterma dimana IMC menjadi tebal apabila semakin lama dikenakan penuaan isoterma.

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LIST OF ABBREVIATIONS

Ag	Silver
Au	Gold
CTE	Coefficients of Thermal Expansion
Cu	Copper
ENIG	Electroless Nickel / Immersion Gold
IC	Integrated Circuit
IMC	Intermetallic Compound
Ni	Nickel
PCB	Printed Circuit Board
SEM	Scanning Electron Microscopy
SMD	Surface Mount Device
Sn	Tin
TAB	Tape automated bonding
UV	Ultraviolet

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Printed circuit boards (PCB) are electronic circuits that are created by mounting electronic components on a nonconductive board, and produce conductive connections between them. The creation of circuit patterns is accomplished using both additive and subtractive methods. The conductive circuit generally is a copper, although aluminum, nickel, chrome, and other metals are sometimes used. The majority of printed circuit boards today are made from purchased laminate material with copper already applied to both sides. Copper that is unwanted for the board will be removed by various methods leaving only the desired copper traces, this is called subtractive. PCB can also be produced using an additive method where traces are added to the bare substrate and this is a complex process of multiple electroplating steps.

The performance and reliability of an electronic product depends largely on the electronic packaging. Electronic packaging is the manufacturing step that packages a semiconductor chip so it is protected and can be connected to other electronic components in electronic equipment. Thus, it is the bridge that interconnects the system to the next level. The interconnection bonding technologies used in electronic packaging has been evolving from wire bonding, tape automated bonding (TAB) to the latest flip-chip interconnection bonding.

Soldering is a process in which two or more metal items are joined together by melting and flow a filler metal (solder) into the joint. The filler metal which has a lower melting point than the work piece will flowing into the joint and solidify to join the metals. For the types of solder, lead free solder Sn-4Ag-0.5Cu is used due to its environmental friendly.

Among the factors that are important to ensure the strength and reliability of the solder joint is the intermetallic compound (IMC) that is formed during soldering. The IMC is formed between the solder and substrate surface finish and functions to provide mechanical, thermal, and electrical connections through the solder joint.

The IMC formation in the solder joint depends on the substrate surface finish metallization and the solder alloy used. The purpose of surface finish is to protect the substrate base metal from oxidizing and limits the diffusion of solder into underlying metal. There are many types of surface finish systems that exist in PCB manufacturing and the most practiced by industry is electroless nickel / immersion gold (ENIG). ENIG is a surface finish that consists of a thick layer of electroless nickel on the top of copper substrate and a thin layer of gold on the top of nickel surface. ENIG mostly used in industry because it offers better planarity, improved corrosion resistance to the base material and excellent wettability.

1.2 OBJECTIVES

The main objective of this research is to determine the effect of coating type on intermetallic compound thickness. Coating is essential in printed circuit board application since it can protect the base material, which is Copper, from oxidation and degradation. However, the coating thickness will give different effect on solder joint strength or life. Therefore, the current work will focus different coating type on solder joint, specifically in intermetallic compound thickness.

1.3 SCOPE

The copper substrates are plated with Electroless Nickel and Electroless Nickel / Immersion Gold (ENIG) surface finish. The substrate then will be forming a solder bump on surface finish by using lead-free solder (Sn-3Ag-0.5Cu) SAC 305. The solder joints produced are then subjected to isothermal ageing for several durations. The IMCs formed are examined using different characterization tools.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter will provide an overview of electronic packaging, printed circuit board, intermetallic compound (IMC), surface finishes which is focus on electroless nickel and electroless nickel/ immersion gold (ENIG), soldering, solder alloy and also solder joint fatigue.

2.2 ELECTRONIC PACKAGING

Electronic Packaging refers to the method of enclosing, protecting or providing physical structure to either electronic components, assemblies of components or finished electronic devices. Packaging is the bridge that interconnects the ICs and other components into a system-level board to form electronic products. The integration of many circuits or components on a single chip is defined as an integrated circuit (IC). ICs are classified by their material and composition, number of transistor elements, degree of integration, manufacturing method, principles of operation and device type. An IC can be a single component such as a power amplifier or they can have many components such as a fully integrated microprocessor used in modern PCs and high performance servers and workstations. IC or chip is packaged into an electronic packaging consisting of a small black epoxy encasement that allows the device to be handled without damaging it and to be soldered onto a circuit board.

Electronics packaging often involves a series of different electronics packages. For example, a series of integrated circuits which each of it is in their own electronics package, are soldered onto a circuit board along with other devices, such as resistor, diode and amplifier, which each of it also in their own electronics package. The circuit board itself also can be considered an electronics package as well, as it provides a place and method to connect the integrated circuits, diodes and resistors as well as a stable structure that can be attached to a framework. The framework, too, is an electronics package, because it’s providing the structure needed to collect the circuit boards into a larger and single assembly. On the smaller end of the scale, primary electronic components such as resistors and CPU chips are usually packaged in plastic or epoxy, and sometimes glass also is used for it. If the component emits interference or is required to endure high temperatures, it can be placed in an additional outer electronic package made of metal. An important part of packaging primary electronic components is the means that the package provides for connecting the components to other components (Tummala, 2001).

Circuit board itself also can be electronic package. The type of package used usually is determined by the use of the assembly or the conditions in which it will be used. For example, a circuit board can be screwed onto a framework that simply holds it in place or be encased in plastic or resin in order to make it waterproof. It can also be enclosed in a sheet, cast or machined metal case to prevent it from being affected by circuit noise, or the case can be airtight to create a hermetic seal that prevents the assembly from being affected by atmospheric conditions.

2.3 PRINTED CIRCUIT BOARD (PCB)

PCB is a self-contained module of interconnected electronic components found in devices ranging from common pagers, or beepers, and radios to sophisticated radar and computer systems. The circuits are formed by a thin layer of conducting material deposited, or "printed," on the surface of an insulating board known as the substrate. Individual electronic components are placing on the surface of the substrate and soldering to the interconnecting circuits. There are three major types of printed circuit board construction which is single-side, double-side, and multi-layer. (Babak, 2005)

Single-side boards have the components on one side of the substrate. When the number of components becomes too much for a single-side board, a double-side board may be used. Electrical connections between the circuits on each side are made by drilling holes through the substrate in appropriate locations and plating the inside of the holes with a conducting material. The third type, a multi-layer board, has a substrate made up of layers of printed circuits separated by layers of insulation. The components on the surface connect through plated holes drilled down to the appropriate circuit layer. The base material for printed circuit board is generally fiberglass, and the conductive connections are generally copper and are made through an etching process (Babak,2005). Table 2.1 shows the steps of manufacturing process for PCB.

Table 2.1: Manufacturing Process for PCB

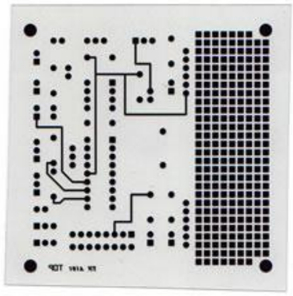
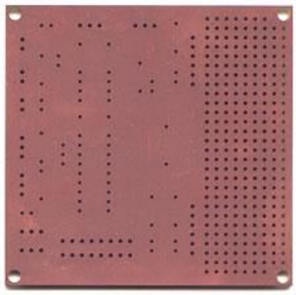
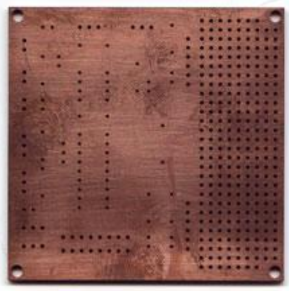
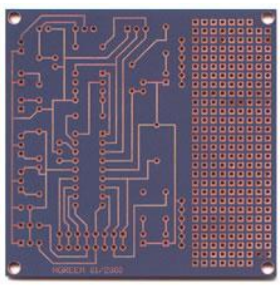
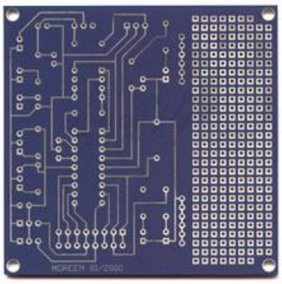
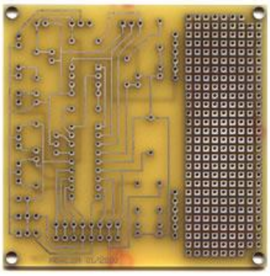
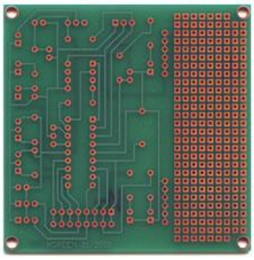
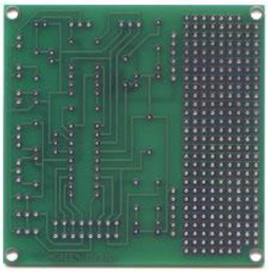
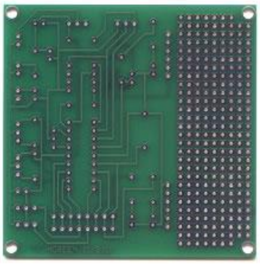
Step	Description	Picture
Step 1: Film Generation	The film is generated from the design files (Gerber files) which are sent to the manufacturing house. One film is generated per layer.	
Step 2: Raw Material	Using industry standard 0.059" thick, copper clad with two sides. Panels will be sheared to accommodate many boards.	
Step 3: Drill Holes	Using CNC machines and carbide drills to drill holes according to the drill spec sent to the manufacturing house.	
Step 4: Electroless Copper	Apply thin copper deposit in holes barrels.	
Step 5: Apply Image	Applying photosensitive dryfilm (plate resist) to panel. Using light source and film to expose panel. Develop selected areas from panel.	

Table 2.1 Continued; Manufacturing Process for PCB

Step 6: Pattern Plate	Doing an Electrochemical process to build copper in the holes and on the trace areas. Apply tin to surface.	
Step 7: Strip and Etch	Remove the dry film, and then etching the exposed copper. The tin protects the copper circuitry from being etched away.	
Step 8: Solder Mask	Applying a solder mask area to the entire board with the exception of solder pads.	
Step 9: Solder Coat	Applying solder to pads by immersing into tank of solder. Hot air knives level the solder when removed it from the tank.	
Step 10: Nomenclature	Applying white letter markings using screen printing process	

Source: Babak Kia (2005)

2.4 ELECTROLESS NICKEL

Electroless is a chemical process which promotes continuous deposition of a metal onto a surface through an oxidation-reduction chemical reaction, without the use of an external electrical potential. An internal reducing agent donates electrons to the positively charged metal ions in solution, thereby reducing the metal and promoting its deposition onto the catalyzed metal surfaces of the substrate. This reaction is considered auto-catalytic because it will continue to plate in the presence of source metal ions and a reducing agent until the board is removed from the plating bath. This gives the plated part a very uniform deposit and the plating thickness can be controlled easily, even on complex shapes and internals (Okinaka, 1974).

Therefore, electroless nickel is the autocatalytic deposition of nickel from an aqueous nickel salt solution onto a substrate and the corresponding oxidation of hypophosphite anions to phosphite ions with the evolution of hydrogen gas at the catalytic surface

The purposes of electroless nickel plating are to improving the corrosion resistance, providing a uniform and dense coating, increasing the surface hardness of the material, and in many cases, maintains the same surface finish the material had before plating.

Electroplating bath consists of a series of components to produce a desired layer of nickel thickness as shown below:

a) Source of nickel ions

   The metal source serves as the provider of nickel ions. It is introduced as metal salts and the most widely used and preferred source of nickel is nickel sulphate. Other nickel salts include nickel chloride, nickel acetate and the ideal source of nickel ions is nickel salt of hypophosphorus acid, Ni $(H_2PO_2)_2$.

b) Reducing agent

   Reducing agents for electroless nickel plating are usually phosphate or boron based with the former more widely used. The reducing agents provide reaction energy for the nickel to deposit.

c) Complexing agent

Complexing agents assist in preventing the pH of the electroless nickel solution from decreasing too fast. They are also required to prevent precipitation of nickel salts into precipitated phosphites and reduce the concentration of free nickel ions. There are several types of complexing agents used and they include citrate, glycolate or lactate ions which come in monodendate, bidendate, tridendate and quadridentate forms of anions. The rate of the nickel deposition is proportional to the stability constant of the complexing agent. The lower plating bath is generally explained by the 'tying-up' process of the nickel ions and releases only a small fraction of free nickel ions.

d) Stabilizer

Stabilizers are added to reduce the spontaneous decomposition rate of the Electroless Nickel plating solution. Stabilizers raise issues of decreased deposition rate of the plating process. Many Electroless Nickel plating processes have employed stabilizers which can be divided into the following groups (Mallory, 1990):

i. Compound of group VI elements
ii. Compound Containing oxygen
iii. Heave metal cations
iv. Unsaturated organic acids

e) pH adjuster

Rapid increase of the hydrogen ion concentration in the plating bath will increase the acidity of the bath. This can be measured by the decrease of the pH value. Reduced pH will slow down the plating rate considerably and eventually stop the plating. The impairing of hypophosphite reduction power in low pH condition causes this condition. In addition, the newly plated nickel deposition will dissolve into the highly acidic plating solution at an increasing dissolution rate and eventually equal the nickel deposition rate. Therefore, it is necessary to adjust and maintain the pH value throughout the plating process in order to obtain a satisfactory thickness (Pecht, 1990). The adjustment of pH can be done by periodic or continuous addition of a soluble alkali hydroxide or a soluble alkaline salt.

Figure 2.1 shows the formation of Nickel ions when Copper substrate was subjected with Electroless Nickel plating. Nickel ions will form a Nickel layer and coat the Copper substrate.

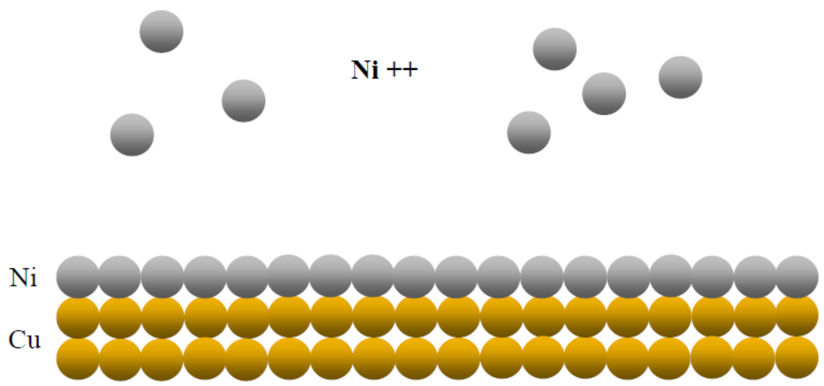


Figure 2.1: Electroless Nickel Plating

Source: Dan Slocum (2003)

2.5 ELECTROLESS NICKEL / IMMERSION GOLD (ENIG)

ENIG is an electroless nickel layer capped with a thin layer of immersion gold. It is a multifunctional surface finish, which is applicable to soldering, aluminum wire bonding, press fit connections, and also as a contact surface. The immersion gold protects the underlying nickel from oxidation or passivation over its intended life. The gold layer is very thin and not intended to provide the main structure of the track. It just acts as a protective coating for the nickel to prevent it tarnishing before it is soldered. Gold is extremely resistant to corrosion so ENIG has several good points. It can be touched with bare fingers without tarnishing, has a very long shelf life, and the pads or tracks are very flat and square-edged, which is something that very important for fine pitch surface mount part.

ENIG is formed by the deposition of electroless nickel on a catalyzed copper surface followed by a thin layer of immersion gold. The IPC ENIG Specification 4522 specifies that the electroless nickel thickness shall be 3 to 6 µm. The minimum immersion gold thickness shall be 0.05 μm which are at four sigma (standard deviation) below the mean, the typical range is 0.075 to 0.125 μm. Higher gold thickness would normally require extended solution dwell time and /or increased solution temperature (Dan, 2003).

The ENIG deposition process is fairly complex; it requires a clean copper surface free of solder mask residues as well as free of any copper/tin intermetallic (tin is used as an etch resist and is stripped before ENIG). Solder mask for ENIG plating must be adherent and completely cured (cross-linked) to withstand the high temperature and prolonged dwell in the electroless nickel bath and in the immersion gold bath (Dan,2003). Figure 2.2 shows the formation of Nickel ions and gold ions when Copper substrate was subjected to the ENIG plating.

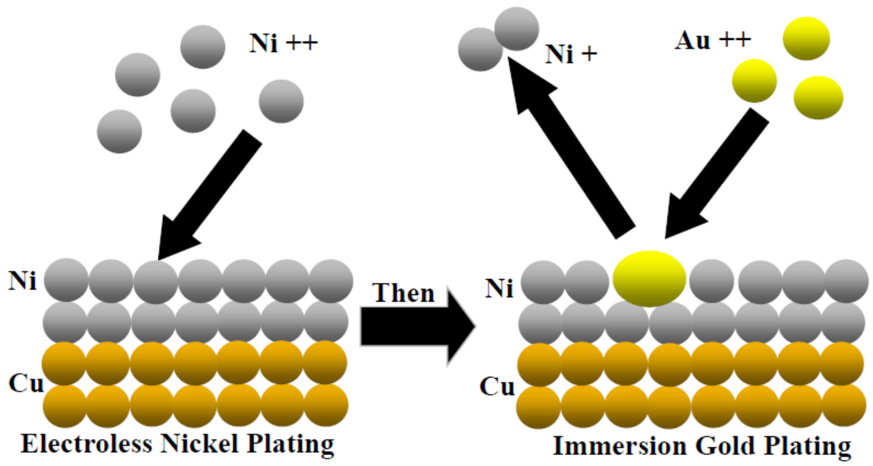


Figure 2.2: Electroless Nickel / Immersion Gold Plating

Source: Dan Slocum (2003)

2.6 INTERMETALLIC COMPOUND (IMC)

IMC have often been observed at or near the solder/substrate interface as well as in the interior of solder joints. Its can be defined as a mixture in specifics proportion of two metallic elements that form a periodic crystalline structure different from those of the original elements. Unlike conventional metal alloys, the particular structure of intermetallic compounds is caused because of the respectively larger strength of bounding between the respective unlike atoms than between like atoms. This particular structure of intermetallic compounds gives them some mechanical properties such as high melting points and great strength (particularly at high temperatures), but poor ductility (Sandström, 2002).

Intermetallic compounds usually form between two metal elements that comprise of a limited mutual solubility through diffusion. These compounds possess a composition of a certain stoichiometric ratio of the two elements (Gilleo, 2004). The new composition has a different crystal structure from those of their elemental components. The interface of tin and copper when examined in a cross section would reveal a superimposed layer consisting of compounds having certain copper/tin ratio as shown in Figure 2.3.

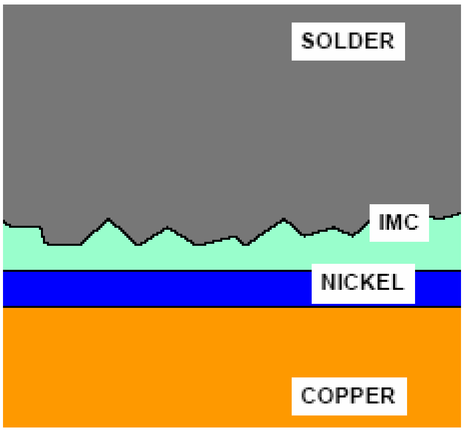


Figure 2.3: Formation of IMC layer between solder and copper

Source: Madeni (2003)

There are some key facts about intermetallic formations that should be illustrated in order to prevent reductions in reliability, solderability and yield. Intermetallics are necessary, but it can result in embrittled joints and unsolderable components or circuit boards.

When solder comes in contact with a common metal substrate for a sufficient amount of time at a high enough temperature, intermetallic compounds may form. Below a solder’s liquidus temperature, formation is primarily a solid state diffusion process and thus depends highly on temperature and time. While solder is in a molten state, the solubility of the element from substrate into molten solder accelerates the rate of intermetallic formation.

There are various factors which influence the intermetallic formation, the composition of the compound and its morphology:

i. The metallurgical reactivity of a solder with a substrate
ii. Soldering (reflow) peak temperature
iii. Dwell time at peak temperature
iv. The surface condition of a substrate
v. The post- soldering storage and service conditions

Apart from above factors, the selection of solder alloy and surface finish play important role as well.

2.6.1 Types of IMC formations in Solder Joints

Formation of IMC at the solder interface is primarily governed by the material of the solder, surface finish and substrate metal pad. The most commonly found IMCs are from copper-tin lead-frame, where the copper is the base material and the tin comes from solders. Lead rarely forms intermetallic in solder joints but commonly encountered elements that may form IMC with tin which include copper, nickel, silver and gold.

The possible IMC forms at the interfacial of solder and substrate is determined by solder material used, substrate material and surface finish covered on the substrate. Table 2.2 shows the possible intermetallic phases in various lead frame system.

Table 2.2: Possible intermetallic phases in various lead-frame system

Lead-frame system	Intermetallic
Copper-tin	Cu_3Sn, Cu_6Sn_5
Nickel-tin	Ni_3Sn_2,Ni_3Sn_4,Ni_3Sn
Gold-tin	AuSn,$AuSn_3$,$AuSn_4$
Silver-tin (Lead-free solder)	Ag_3Sn

Source: Madeni (2003)

The most common solder/substrate intermetallic compound is tin/copper (Sn/Cu). The growth of the total intermetallic layer is influenced by the synergy information and growth between η (Cu_6Sn_5) and ε (Cu_3Sn) phases. Cu_6Sn_5 (η- phase) is the first to form at lower temperatures (< 170°C) and is essential for good solder adhesion to the copper substrate. This compound grows rapidly but once the metals solidify, it will slow sharply. The ε-phase has been shown to grow at the expense of the η-phase, and has higher activation energy of formation, so growth of ε is more predominant at higher temperatures. The mechanisms for intermetallic formation are also greatly influenced by the interdiffusion characteristics of tin and copper.

In Nickel/gold-tin system, the eutectic solder forms a strong attachment to underlying nickel by forming the Ni_3Sn_2, Ni_3Sn_4, Ni_3Sn intermetallic while the Au dissolves into the molten solder, and forms fine, needle-shaped $AuSn_4$ intermetallic precipitates that are retained in a dense distribution in the bulk of the solder joint after it has solidified (Glazer, 1991).

When lead free solder, such as Sn/Ag or pure Sn is used on a copper substrate, the Ag_3Sn plate intermetallic is formed while Cu_6Sn_5 compound forms as the bottom layer. Large Ag_3Sn plate formation is found to be substantially reduced in alloys with a silver content less than 3 wt % (Sung, 2004). Because of the relatively low fraction (3-5 wt%) of alloying elements, these intermetallic structures comprising a small portion of the area within the solder joint. The morphology are varies, exhibiting a round, lath like, blocky, or needle like structure. Studies have shown, however, that intermetallic structures at the interface, such as tin-copper, grow slower in some tin-based lead-free solders than with their leaded counterpart. It is believed that lead plays a part in enhancing intermetallic growth when subjected to thermal exposure.

2.7 SOLDERING

Soldering is a process in which two or more metal items are joined together by melting and flow a filler metal (solder) into the joint, the filler metal having a lower melting point than the workpiece. Soldering basically is use to make electrical connection between electrical device like transistor, diodes, capacitors, resistance and etc. Its also provide physical connection between the component and its supporting printed circuit board (Woodgate, 1983).

Solder chemically reacts with other metals to form different alloy. There are four basic element involve in soldering process; base metal, flux, solder and heat. A base metal is a metal that contacts the solder and forms an intermediate alloy. When attaching electronic components to a printed circuit board, the component's leads or pins and board's metallic circuitry at the base metals and will contact with the solder. Many metals, such as copper, bronze, silver, brass, and some steels, readily react with solder to form strong chemical and physical bonds. There is a direct relationship with the level of surface oxidation on the base metal and how readily solder will react with it. The more oxidation is present, the weaker the solder bond will be (Hwang, 2002).

Flux is often applied as a liquid to the surface of the base metals prior to soldering. The first and primary purpose of flux is to stop the base metals from oxidizing while they are being heated to the soldering temperature. The flux covers the surface to be soldered, shielding it from oxygen and thereby preventing oxidation during heating. Most fluxes have an acidic element that is used to remove the oxidation already present on the base metal. Using a strong acid, it would be possible to virtually completely clean off the oxidation layer. When the liquid solder is applied, the flux must readily to move out of the way so the solder can come directly contact with the base metal. During this process some of the flux inevitably combines with the solder.

Solder is typically transported and sold in solid form. Common forms of solder including chips, bars, and wire (often with a core of flux), each of it which has advantages in different soldering processes. A common process called reflow soldering is use for a solder paste. Solder paste is a substance with a cream-like consistency made up of solder, flux, and some carrying medium. The material most commonly used for solder in the electronics industry is a tin-lead alloy. Tin-lead alloys have relatively low melting point and can be produced at a low cost in comparison with other alloys with similar properties.

2.7.1 Soldering Methods

There are various soldering techniques developed throughout the growth of electronic assembly to promote the process capability and productivity. It will be categorized whether it is performed by hand or by machine. For circuit board, generally the soldering process will fall into two main categories, which are wave soldering and reflow soldering. For wave soldering, it is primarily used for soldering through-hole components on PCBs where the electronic components are inserted prior to application of solder. For reflow soldering, it is used for soldering SMD (Surface Mount Device) components on to PCBs. The electronic components are mounted after the application of solder.